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Influence of thermal oxidation on the properties of titanium alloys

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Abstract. In this study, the effect of thermal oxidation on the properties of the surface of titanium alloys was examined. Thermal oxidation was carried out at 750 °C within 6 hours, 800 °C within 5 hours, and 850 °C within 4 hours. Electrical resistance of the surface after thermal oxidation was measured. Metallographic analysis, microprobe analysis and X-ray phase analysis were carried out to determine the structure, chemical and phase compound of the oxide layer on the surface of titanium alloys after thermal oxidation. The results indicate that thermal oxidation leads to increase of electrical resistance of the surface of titanium alloys. Microstructural analysis showed that thickness of the oxide layer after thermal oxidation is in the range of 25 to 100 μm. Microprobe and X-ray phase analysis showed that TiO_2 and Al_2O_3 oxides have the best impact on electrical resistance. Two variants of possible application of the results have been presented.

1. Introduction

Thermal oxidation is a well-known method of titanium alloys surface properties modifying. Dense oxide layer occurs on the surface of titanium alloys after thermal oxidation. This layer is characterized by increased hardness [1], high corrosion resistance [2], good biotribological properties [1, 3] and high wear resistance [4]. This leads to widespread use of titanium alloys with oxide coatings in prosthetics and medicine and in chemical engineering. At the same time electrical properties of oxide layers grown by thermal oxidation on the surface of the titanium alloys are still insufficiently explored. Although high dielectric properties of TiO_2 (rutile) have been studied in [5–7]. Very large variation of the results was observed in studying the electrical resistance of the oxide layers on titanium, therefore only data on the distribution of the electrical resistance at the cross-section of the oxide layer is published in literature. It is believed that heating of titanium alloys at temperatures above 900 °C leads to the nominal stoichiometric composition of rutile crystals. It is confirmed by high electrical resistance above 10^{12} Ohm·cm at room temperature. Pure stoichiometric rutile is an isolator. Electrical conductivity increases in case of deviation from stoichiometric composition. Increase of electrical conductivity continues until the rutile homogeneity boundary is achieved.

Data on the influence of thermal oxidation on the electrical properties of the oxide layer is presented in Table 1 [7]. It is shown that the breakdown voltage of the oxide layer increased with the thickness of the layer, therefore oxide layer with dielectric properties can be formed on the surface of titanium alloys under certain conditions. Investigation of the microstructure of the oxide layer is also necessary because of the dependence of the electrical properties on the thickness of oxide layer. The presence of TiO_2, Al_2O_3 and other oxides, which have electrical resistance close to dielectric, in the compound of the oxide layer causes its high electrical resistance [8]. Thus, studying chemical and phase composition of the oxide layer on the surface of the titanium alloys is of scientific interest.

Table 1. Influence of heat treating on the dielectric strength of the oxide layer in commercially pure titanium.

Temperature, ˚C	Time, hours	Thickness of oxide layer, μm	Breakdown voltage, V
600	25	4	60
	100	7	130
	500	19	400
	1000	22	460
700	25	10	200
	100	25	500
	250	30	600

The purpose of the presented work was to study the electrical resistance of thermally oxidized titanium alloys, microstructure, phase, and chemical compound of the oxide layer. The application of thermally oxidized titanium alloys is described in the presented article.

2. Materials and methods

The measurements were made on titanium alloys Grade2, OT4-1, OT4, VT5, Grade6, PT-7M, Grade5, VT3-1, VST5553. Samples from these alloys with dimensions 40×20×5 mm after rolling were studied. Samples were subjected to thermal oxidation at 750 °C within 6 hours, 800 °C within 5 hours, and 850 °C within 4 hours.

Electrical resistance of the oxide layer was measured with ohmmeter Sonel MIC-1000 at the voltage of 50 V. Metallographic study was carried out to determine the structure of the oxide layer. The samples were polished on Struers LaboPol-1 and then etched using a composition of 50 % HF + 50 % glycerol. Microstructures were obtained with the optical microscope Olympus GX51equipped with Siams 700 system. Microprobe analysis was conducted using scanning electron microscope Jeol JSM 6490LV equipped with an attachment for energy-dispersive electron microprobe analysis Inca DryCool with a resolution of 130 e V. Analysis of chemical and phase compound of the oxide layer was carried out by X-ray phase analysis using the diffractometer Bruker D8 Advance equipped with a nickel-filtered copper Kα radiation (λ = 1.540 Å). Crystallographic database PDF2007 and software package EVA13.0.0.3 were used to decrypt the diffraction patterns. Semi-quantitative estimation of the phase composition was used to determine the proportion of phases.

3. Results and discussion

3.1. Electrical resistance

The results of measurement of electrical resistance of the titanium alloys after the thermal oxidation are presented in Table 2. The electrical resistance of almost all titanium alloys tends to grow after the thermal oxidation. It should be noted that alloys with vanadium have lower electrical resistance due [9] to formation of a volatile oxide V_2O_5 which has a melting point of 670 °C and lower in case of eutectic compounds formation with oxides of the other metals. The appearance of a liquid phase at the interface between the metal and the oxide leads to acceleration of diffusion of the oxygen and to formation of pores and discontinuities.

Table 2. Electrical resistance of the titanium alloys after the thermal oxidation, Ohm.

Alloy	Temperature of thermal oxidation, ˚C		
	750	800	850
Grade2	0.04×10^{13}	0.72×10^{12}	0.04×10^{13}
OT4-1	0.04×10^{13}	0.04×10^{13}	0.04×10^{13}
OT4	0.56×10^{12}	0.16×10^{12}	0.04×10^{13}
VT5	0.4×10^{11}	0.6×10^{12}	0.16×10^{11}
Grade6	0.88×10^{12}	10^{12}	0.84×10^{10}
PT-7M	10^{8}	0.6×10^{10}	0.04×10^{13}
Grade5	0.4×10^{7}	0.65×10^{7}	10^{9}
VT3-1	0.28×10^{10}	0.3×10^{11}	10^{11}
VST5553	0.36×10^{8}	0.45×10^{8}	0.36×10^{8}

Grade 6 titanium alloy which contains 2.5 % of tin also has lower electrical resistance. TiO_2, TiO and pure tin were observed between the metal and the oxide layer on Grade6 in [9]. Tin has a low electrical resistance and its presence in the oxide layer leads to decrease of electrical resistance.

It can be concluded that the aluminum in an amount of 2–4 % leads to a decrease of electrical resistance, but electrical resistance increases when amount of aluminum is more than 4 %. The greatest electrical resistance is observed in the alloys with an aluminum content of 0.8–1.5 % and manganese content of 0.8–1 %. A positive effect may be noted on the electrical resistance of zirconium and niobium at the oxidation temperature of over 800 °C. This is confirmed by studies of PT7M (Ti-2, 2Al-2, 5Zr) and Ti-6Al-7Nb respectively.

It follows from the above that TiO_2 lattice has both electron and hole conductivity. Alloying of rutile by the elements with a valence greater than 5 leads to ionisation. Alloying element transmits the electron to rutile and it leads to n-type conductivity and lower electrical resistance. Conversely alloying of rutile by the elements which have a valence lower than 4 leads to transmitting of the electron from rutile to the acceptor. This causes p-type conductivity and growth of electrical resistance [10]. Thus, we have shown that the thermal oxidation leads to growth of electrical resistance of the titanium alloys. It confirms the hypothesis which are presented in [5, 7].

3.2. Results of microstructural and microprobe analysis

One of photomicrographs of oxide layer on the surface of some titanium alloys after thermal oxidation, obtained with an optical microscope Olympus GX51, are presented in Figure 1. Thickness of oxide layer on most alloys is in the range of 10 to 100 μm. Microstructural studies have shown that a homogeneous layer consisting of dark and light regions is formed on the surface of most titanium alloys after thermal oxidation.

Results of microprobe analysis which are shown in Figure 2 confirm the hypothesis of the presence of several layers with different chemical compositions in the oxide layer.

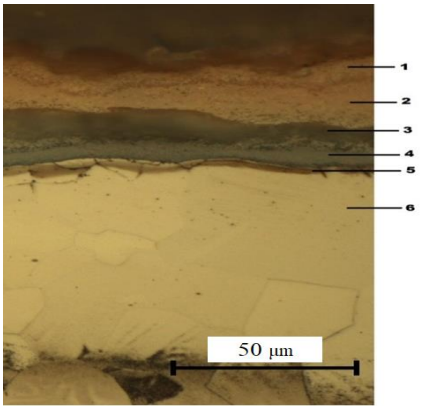
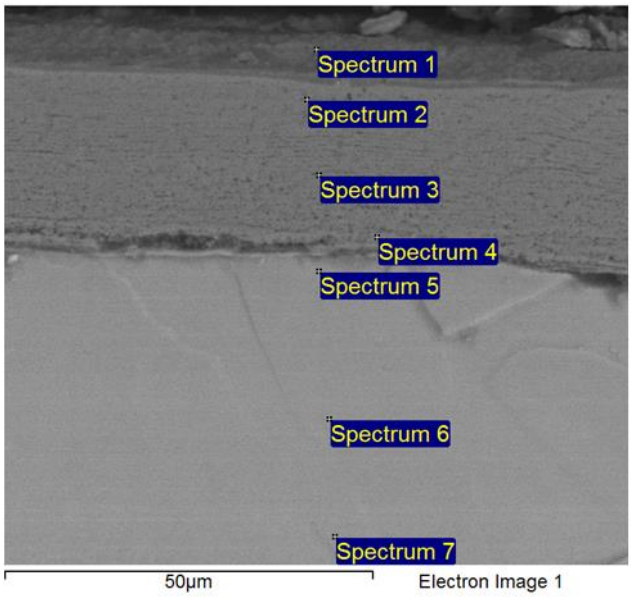


Figure 1. Photomicrograph of oxide layer on surface of titanium alloy VT5 after thermal oxidatic 850 °C:
1. Outer layer enriched with aluminum oxide Al_2O_3;
2. The layer consists of TiO_2.
3. The layer consists of non-stoichiometric oxide the titanium, for example, $TiO_{1,9}$.
4. The layer at the interface with the metal consist intermetallic alloying elements displaced from oxide layer by diffusing oxygen.
5. Undefined layer.
6. The diffusion layer saturated by oxygen.



Spectrum	In stats.	O	Al	Si	Ti	Zr	Total
Spectrum 1	Yes	53.51	5.90	1.11	39.47		100.00
Spectrum 2	Yes	41.48	6.55		50.31	1.66	100.00
Spectrum 3	Yes	37.88	0.29		59.92	1.90	100.00
Spectrum 4	Yes	38.73	0.00		59.66	1.61	100.00
Spectrum 5	Yes	12.56	1.72		83.21	2.52	100.00
Spectrum 6	Yes	2.34	1.89		92.99	2.78	100.00
Spectrum 7	Yes	3.39	2.12		92.35	2.14	100.00

Figure 2. Chemical composition of PT-7M after thermal oxidation at 850 C.

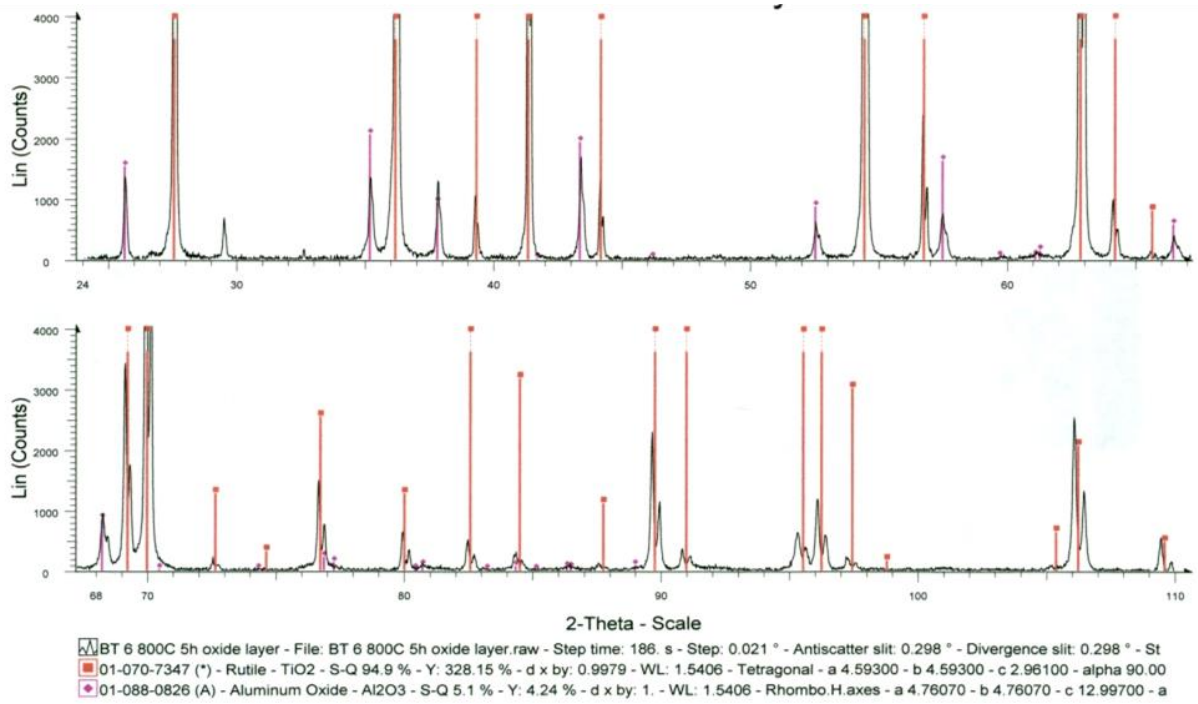


Figure 3. Diffraction pattern of the oxide layer on the surface of titanium alloy Grade5 after thermal oxidation at 800 °C during 5 hours.

3.3. Results of X-ray phase analysis

Diffraction patterns obtained by X-ray phase analysis of the oxide layer are presented in Figure 3. Results of decrypting of the diffraction patterns are presented in Table 3.

It can be concluded from Table 3 that the main component of the oxide layer is rutile (TiO_2). TiO and Ti_6O are transitional oxides which can be frequently found in the oxide layer. Their electrical

resistance is significantly lower than that of rutile. Also here are aluminum oxide Al_2O_3 in the oxide layer on the surface of all alloys which contain more than 4 % of aluminum except VST5553. It is impossible to explain its absence in the oxide layer on VST5553. Consequently, oxides that have high electrical resistance are presented in the oxide layers of all titanium alloys.

Table 3. Chemical composition of the oxide layer on the surface of titanium alloys after thermal oxidation.

Titanium alloy	Temperature of thermal oxidation, °C	Oxide	Content, %	Type of the lattice
Grade2	800	TiO_2	95.2	Tetragonal
		TiO_2	0.6	Monoclinic
		Ti_6O	0.9	Hexagonal
		$TiO_{0,857}$	3.3	Cubic
OT4	800	TiO_2	95.1	Tetragonal
		Al_2O_3	4.6	Rhombic
		Ti_6O	0.3	Hexagonal
OT4	850	TiO_2	87.0	Tetragonal
		Al_2O_3	13.0	Rhombic
OT4-1	850	TiO_2	87.6	Tetragonal
		Al_2O_3	12.4	Rhombic
Grade6	850	TiO_2	52.4	Tetragonal
		Al_2O_3	22.9	Rhombic
		Ti_6O	24.7	Hexagonal
PT-7M	850	TiO_2	81.7	Tetragonal
		Al_2O_3	18.3	Rhombic
Grade5	800	TiO_2	94.9	Tetragonal
		Al_2O_3	5.1	Rhombic
VT3-1	800	TiO_2	90.5	Tetragonal
		Al_2O_3	4.6	Rhombic
		Ti_6O	5.0	Hexagonal
VST 5553	750	TiO_2	95.5	Tetragonal
		Ti_6O	4.2	Hexagonal
		TiO	0.3	Tetragonal

Despite high content of vanadium in Grade5 and VST5553 its oxides were not observed in the oxide layer on the surface of these alloys. It could be explained by the volatility of the vanadium oxides when heated. Oxides of molybdenum and chromium are not detected in the oxide layer.

It should be noted that X-ray phase analysis doesn't allow to determine the presence or absence of a certain element in the studied sample, if it doesn't form its own phase in sufficient quantity. Consequently, we can't discard the possibility of the presence of the alloying elements in the form of solid solution in the oxide layer. For example, the presence of tin in the compound of the oxide layer in Grade6 has not been observed using X-ray phase analysis but it has been observed using other methods in [9].

It follows from the presented results that TiO_2 and Al_2O_3 oxides have the best impact on electrical resistance. Transitional oxides of titanium that could have positive influence on the electrical resistance are also found in the oxide layer. The hypothesis of the positive impact of MnO on the electrical resistance of OT4 titanium alloy after thermal oxidation was not confirmed.

4. Conclusions

The present work covers the effect of thermal oxidation on the electrical resistance, microstructure and chemical compound of the oxide layer. It is shown that:

1. Thermal oxidation leads to increase of the electrical resistance up to 1 TOhm.

2. Aluminum in the titanium alloy in an amount of 2–4 % leads to a decrease in electrical resistance, but electrical resistance increases when the amount of aluminum is more than 4 %.

3. Vanadium in the titanium alloy leads to lower electrical resistance due to volatility of V2O5 when heated.

4. Microstructural analysis showed that thickness of the oxide layer after thermal oxidation is in the range of 25 to 100 μm. The oxide layer consists of several regions situated one over the other that differ in a chemical compound. It is confirmed by the microprobe analysis.

5. The study of the chemical composition of the oxide layer by X-ray phase analysis has shown that the oxide layer consists mainly of rutile (TiO_2), corundum (Al_2O_3), transitional oxides of the titanium (Ti_6O, TiO).

It is necessary to focus on the possible application of the presented results. One of the variants of application of the oxidized titanium alloys is the production of semiconductor devices. The oxide layer is created on the surface of the metal and the silicide layer is applied on the oxide layer through heat treatment. This variant is described in [12]. Another interesting variant of application of the presented phenomenon is the application of thermally oxidized parts made from titanium alloys for electrical insulation of cutting tools. It leads to an improvement of tool life up to 2.5 times. This variant is described in [13–15].

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